

## THE RMPROCESS

G. A. WHITE, T. R. ROSZKOWSKI, D. W. STANBRIDGE

THE RALPH M. PARSONS COMPANY

PASADENA, CALIFORNIA 91124

## INTRODUCTION

Current specifications for pipeline gas dictate that most gasification processes require an upgrading of their crude syngas by a stage of methanation. The upgrading reduces the concentration of hydrogen and carbon monoxide while increasing the heating value of each cubic foot of gas. The RMP process has demonstrated an unusual upgrading capability by methanating, without recycle, a crude syngas of approximately 50 percent hydrogen and 50 percent carbon monoxide and containing less than 1 percent methane. The process has exceptionally wide applicability for gases produced by any coal gasification system from near atmospheric pressure to over 1000 psig.

## PROCESS DESCRIPTION

In the process, desulfurized syngas flows through a series of fixed-bed adiabatic catalytic reactors. Between reactors, heat is removed from the system by the generation of high pressure steam in conventional heat exchange equipment. As the flow progresses through the series of reactors and exchangers and the bulk of the syngas is methanated, the temperature of the process gas is progressively lowered, finally resulting in an adequately reduced temperature favorable for achieving a high conversion efficiency of hydrogen and carbon oxides to methane.

The series of reactors and exchangers which methanates a raw syngas without pretreatment other than desulfurization, is collectively termed bulk-methanation. The chemical reactions which occur in bulk methanation, including both shift conversion and methanation are moderated by the addition of steam which establishes the thermodynamic limits for these reactions thereby controlling operating temperatures. The flow sequence through bulk methanation is shown in Figure 1.

## EXAMPLE AT 400 PSIA

The conditions selected for illustration here include desulfurized syngas available at 700°F and 400 psia, consisting of 49.8 percent hydrogen, 49.8 percent carbon monoxide, 0.1 percent carbon dioxide and 0.3 percent methane. As shown in Figure 1, 40 percent of this syngas is mixed with superheated steam and the mixture enters the first bulk methanator at 900°F. The principal reaction occurring in this reactor is shift conversion with only a minor degree of methanation. The first reactor effluent is cooled and mixed with an additional 30 percent of the syngas to give a mixed temperature of 1000°F into the second bulk-methanation reactor. Again the second reactor effluent is cooled by the generation of steam, mixed with the remaining 30 percent of the syngas to give a mixed temperature of 1000°F as feed to the third reactor.

In the fourth, fifth and sixth reactors, the inlet temperatures are controlled at 1000°F, 600°F and 500°F respectively which results in a bulk methanated product-gas whose composition is shown in Figure 2. The operating temperatures and pressures for each reactor in bulk-methanation are also shown in Figure 2. The residual hydrogen content leaving the sixth reactor is less than 10 volume percent on a dry basis. Such a gas can then be methanated in a final "dry" stage following carbon dioxide removal, to reduce the hydrogen content to below 3 percent, and leaving less than 0.1 percent carbon monoxide.

#### EXAMPLE AT LOW PRESSURE

A similar set of design numbers are shown in Figure 3 when operating at near atmospheric pressure. Inlet pressure to the first bulk-methanator reactor is 65 psia and the outlet pressure from the sixth reactor is 22 psia. In this case, the total syngas is introduced into the first bulk-methanation reactor together with the total steam. Because the driving force for methanation is proportionately lower at the lower pressure, the outlet temperature even from the first reactor is below 1400°F. Significantly, leaving the sixth reactor, the hydrogen content of the effluent gas on a dry basis is only 12.1 percent at 22 psia compared to 9.3 percent when operating at 312 psia. This relatively small difference is not entirely surprising in view of the lower operating temperature and the large excess of carbon dioxide present in each case which tends to mask the difference in operating pressure.

#### DESIGN FEATURES

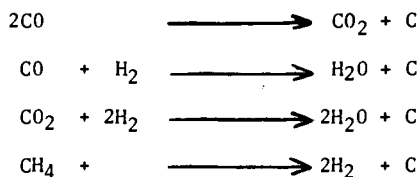
Whether operating at high pressures or low, reactor outlet and inlet temperatures are all conveniently high for the economical generation of 1500 psig steam in conventional heat exchange equipment. Of the total steam produced, approximately one-third is used in the RMP process to accomplish shift conversion, methanation and carbon dioxide regeneration. The mechanical energy of even that portion of the produced steam needed for the operation of the process, will provide a part of the total power requirement of a coal gasification complex by using back pressure turbines. The bulk of the steam produced, approximately two-thirds of the methanation heat, is available as export steam at 1500 psig for any services within a complex.

Now referring back to Figure 1, it is to be noted that there is no separate shift conversion system and no recycle of a product gas for temperature control. Rather, this system is designed to operate adiabatically at elevated temperatures with sufficient steam addition to cause the shift reaction to occur over a nickel catalyst while avoiding carbon formation. The refractory lined reactors contain fixed beds of catalysts and are of conventional designs. The reactors can be a minimum diameter for a given plant capacity since the process gas is once-through only with no recycle, employing less steam than is conventional for shift conversion alone and using a catalyst of a standard ring size of 5/8 x 1/4 inches.

#### AVOIDING ZONES OF CARBON FORMATION

Before proceeding further with methanation into the cleanup stage, it would be well to review some of the design and operating problems which have been experienced by most developers of methanation systems. Specifically, carbon formation and catalyst sintering are two of the more common problems confronting methanation processes. When considering carbon formation, reference is made to its

potential production from carbon oxides and methane as illustrated by the following equations.



The prediction of conditions favorable for the formation of carbon from these sources can be made by straightforward thermodynamic calculations. However, because a number of other chemical reactions can occur simultaneously and since relative reaction rates are not well known, it is useful to know whether a specified mixture of syngas and steam would have a thermodynamic potential for carbon formation when at chemical equilibrium.

To assist in the proper visualization of multiple chemical reactions occurring simultaneously, we have developed a ternary diagram simplified by considering only the concentration levels of the principal chemical elements present in mixtures of syngas and steam. Carbon, hydrogen and oxygen are used as the identifying elements in our system; these elements are located at the three apexes of the ternary diagram shown in Figure 4. A number of chemical compounds are shown on this figure when the elements are appropriately balanced with one another. Hydrocarbons such as methane and butane are on the left of the figure, carbon oxides on the right and water on the base line connecting hydrogen and oxygen.

Figure 5 has superimposed on the ternary, carbon isotherms for a pressure of 30 psia. Interpretation of the isotherms shows that mixtures of the elements which fall above the curves are in the carbon forming region when at chemical equilibrium. Mixtures of the elements which fall below the curves are outside the carbon forming region at equilibrium. Gas mixtures falling within the family of curves should be at an operating temperature that will carry the specified concentration of carbon in the vapor phase.

Figure 6, which represents a family of carbon isotherms at 400 psia, shows that in certain areas of the diagram, elevated temperatures support higher concentrations of carbon in the vapor phase, but in other areas, lower temperatures favor higher concentrations of carbon. So depending upon the element-mix of gases feeding a methanation reactor, an increase in temperature could cause a mixture to approach a condition where carbon could theoretically be formed. Since these figures are based on equilibrium concentrations of chemical compounds, temperature excursions into the carbon formation region may not result automatically in the formation of solid carbon since such reactions may occur at such a slow rate as to be negligible. On the other hand, it is not good practice to design a system that is normally operating under conditions that are theoretically favorable for carbon formation and depend upon kinetics to keep the operation out of trouble.

The mathematical properties of the set of equations describing chemical equilibrium in the synthesis gas system indicate that the carbon producing regions are defined solely by pressure, temperature and elemental analysis. Once a safe blend of reactants has been determined by use of the ternary, the same set of equations which was used to derive the ternary may be used to determine the gas composition.

Figure 2, gives gas compositions which represent proposed operating conditions at the pilot plant. Figure 7 shows where two compositions are located on the ternary diagram relative to the potential for carbon formation: (1) the feed gas composition to the first bulk-methanation reactor and (2) the product composition from the third reactor which then remains a fixed point throughout the remaining reactors since no addition of gas is made beyond the third reactor. From this figure, it can be seen clearly that sufficient steam has been added to move the mixture well outside the carbon formation region. Even after adding the total syngas to the system, it is not theoretically possible to form carbon when the system is at chemical equilibrium.

It will be quickly recognized that feed-gases to most, if not all, methanation systems for SNG production, are theoretically capable of forming carbon. This potential also exists for feed-gases to all first stage shift converters operating in ammonia plants and in hydrogen production plants. However, it has been commercially demonstrated over a period of many years that carbon formation at inlet temperatures to shift converters is a relatively slow reaction and that once shifted, the gas loses its potential for carbon formation. Carbon formation has not been a common problem at the inlet to shift converters and it has been no problem at all in our bench-scale work and it is not anticipated that it will be a problem in our pilot plant operations.

For a clearer understanding of the behavior of syngases in a shift converter, we have established another set of carbon isotherms when considering the shift reaction only (without methanation) in addition to the carbon forming reactions. Figure 8 shows isotherms at a partial pressure of 270 psia for all components of a gas mixture but excluding methane. Figures such as this are helpful when establishing inlet conditions to reactors since operating data from commercial plants can be used as points of reference.

#### CLEAN-UP METHANATION

Returning now to the cleanup stage of methanation, Figure 9 shows a system wherein final methanation occurs following gas cooling and removal of steam, and a reduction of carbon dioxide down to approximately 4 percent. Under these conditions, and at a pressure of 300 psia, residual hydrogen is less than 3 percent and carbon dioxide is less than 2 volume percent of the dry product gas following methanation. When operating at near atmospheric pressure, reduction of steam and carbon dioxide are followed by compression to either an interstage level or to delivery pressure for the final stage of methanation. For all pressure levels, the final stage of methanation is outside the region of carbon formation.

Carbon dioxide can be removed from the effluent gas from bulk methanation by any one of several conventional absorption systems. At this point in the process, the gas that must be treated for carbon dioxide removal is less than half of the volume of a shifted gas from which carbon dioxide is normally removed when preparing a syngas to approach stoichiometric concentrations of reactants for methanation. Finally, the gas would be dried to a nominal 7 pounds of water per million scf of gas.

## CONCLUSION

Advantages of the RMPProcess are related particularly to cost savings in both capital equipment and operating requirements.

1. Shift conversion. The shift reaction and methanation proceed concurrently without interference over bulk-methanation catalyst thereby eliminating the need for a separate shift conversion operation.
2. Steam utilization. Less steam is employed in the RMPProcess than is required for conventional shift conversion even though in other methanation processes as little as one-half of the total syngas is processed through shift conversion to achieve a near-stoichiometric balance of hydrogen and carbon monoxide for methanation.
3. Temperature control. Temperature control is by steam addition. There is no gas recycle and therefore no recycle compressor.
4. Steam production. The RMPProcess operates at temperatures generally above 1000°F providing a large temperature difference for the production of high pressure steam. Because of this, we can produce more steam and produce it at a higher pressure with less heat transfer surface than other processes.
5. Carbon dioxide removal. Aside from contained carbon dioxide which is removed from syngas when absorbing hydrogen sulfide, the total carbon dioxide produced in the methanation system is removed by conventional absorption in a single stage operation where the volume of gas to be treated is a minimum and the partial pressure of the carbon dioxide is a maximum.
6. Low pressure operation. By using the driving force of a large excess of carbon dioxide for methanation when operating at low pressures, bulk methanation can accomplish a high degree of syngas conversion thereby requiring only a single stage of final methanation following compression to meet pipeline SNG specifications. Such an operation reduces the compression duty by reducing the volume of syngas to a fraction of its original volume while still at low pressure.
7. Space velocity. Most of our experimental data has been developed when operating at a wet outlet space velocity of approximately 10,000 volumes per volume per hour. However, we have data at space velocities up to 25,000. The pilot plant will operate in the range of 5,000 when processing 1 million scfd of raw syngas. Operating on a once-through basis without recycle and at the indicated space velocities, catalyst volumes are a minimum compared with other processes when identical over-design factors are used.

Acknowledgement is sincerely made to Catalyst Consulting Services, Inc. of Louisville, Kentucky, in particular to Dr. Harold W. Fleming, for unusual services of the highest quality while directing the bench-scale experimental program which provides the technical basis and support for the RMPProcess.

FIGURE 1 - BULK METHANATION

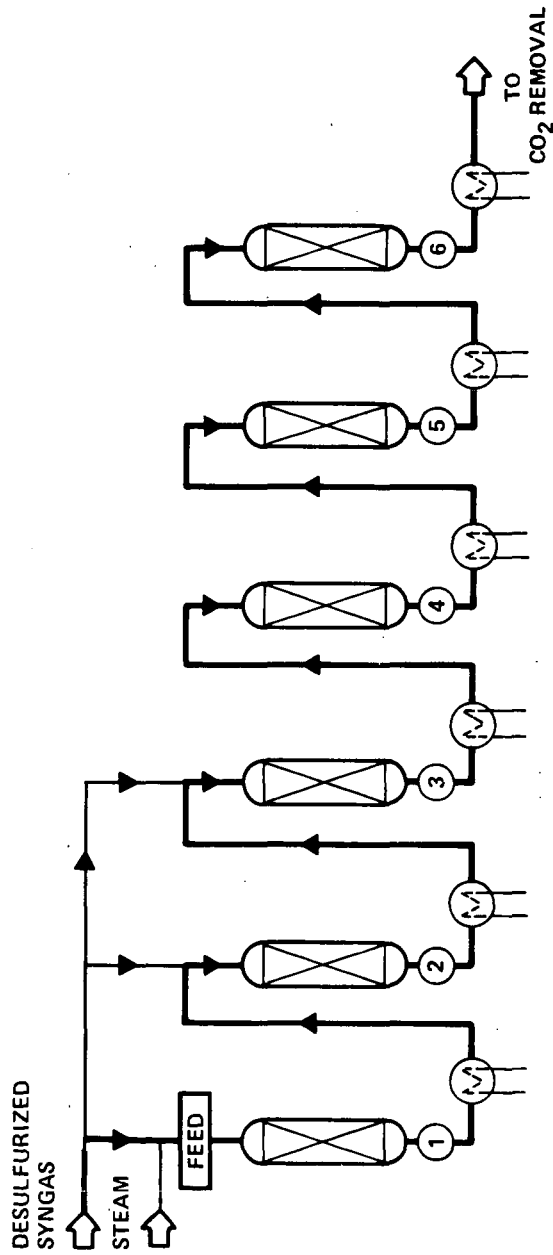


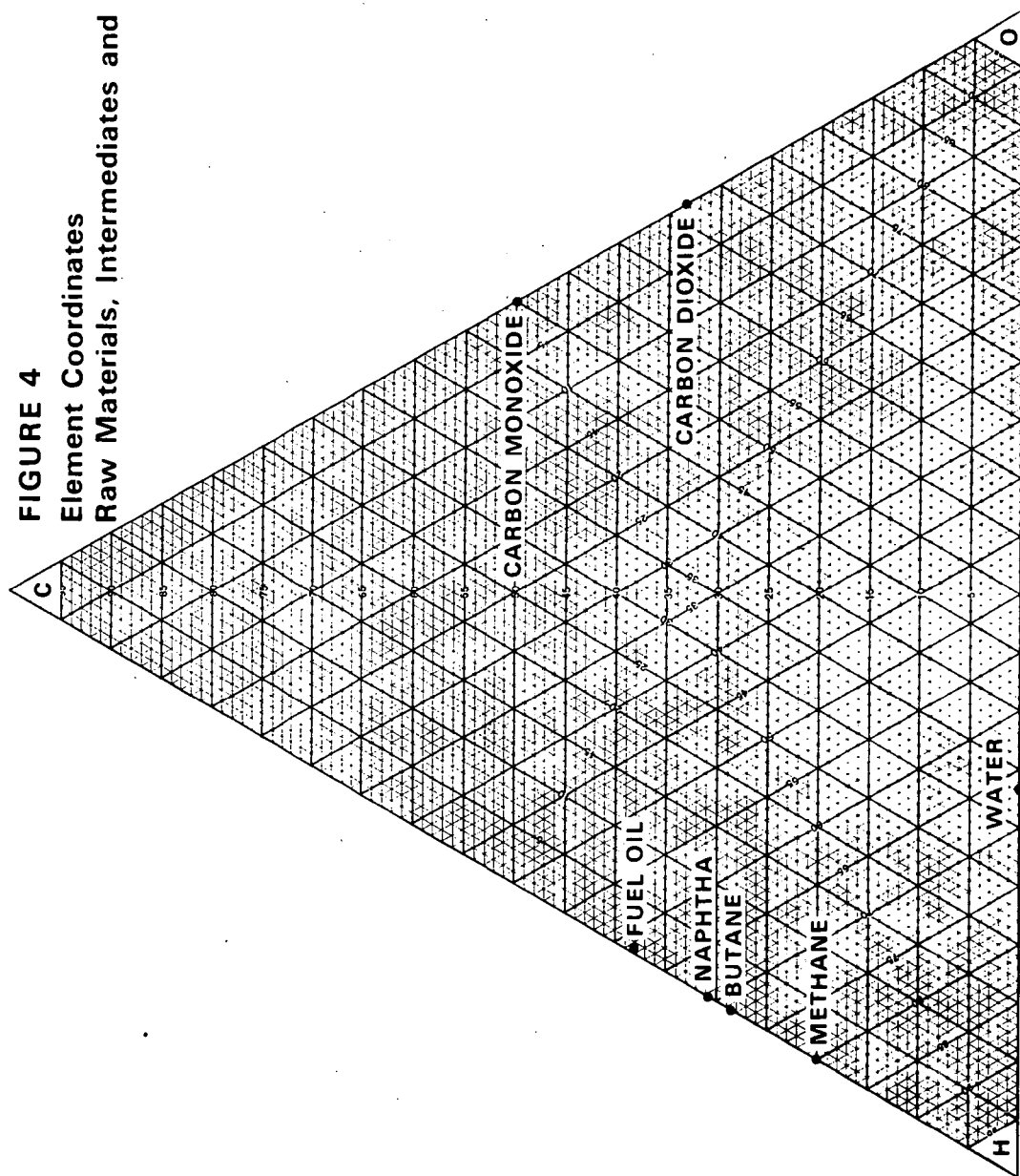
FIGURE 2 - METHANE PRODUCTION @ 400 PSIA

Reactor No.	Feed	-----Outlet-----					
	<u>1</u>	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>	<u>5</u>	<u>6</u>
Composition, Vol %							
H <sub>2</sub>	49.80	54.53	48.07	43.09	36.90	22.86	9.29
CO	49.80	13.97	18.46	20.63	15.25	5.64	.87
CO <sub>2</sub>	0.10	25.80	24.04	23.64	29.21	39.90	46.84
CH <sub>4</sub>	<u>0.30</u>	<u>5.70</u>	<u>9.43</u>	<u>12.64</u>	<u>18.64</u>	<u>31.60</u>	<u>43.00</u>
	100.00	100.00	100.00	100.00	100.00	100.00	100.00
Steam/Gas	1.20	0.88	0.56	0.43	0.50	0.65	0.83
Pressure, psia	397	387	372	357	342	327	312
Temperature °F	900	1424	1434	1423	1322	1119	881

FIGURE 3 - METHANE PRODUCTION @ 65 PSIA

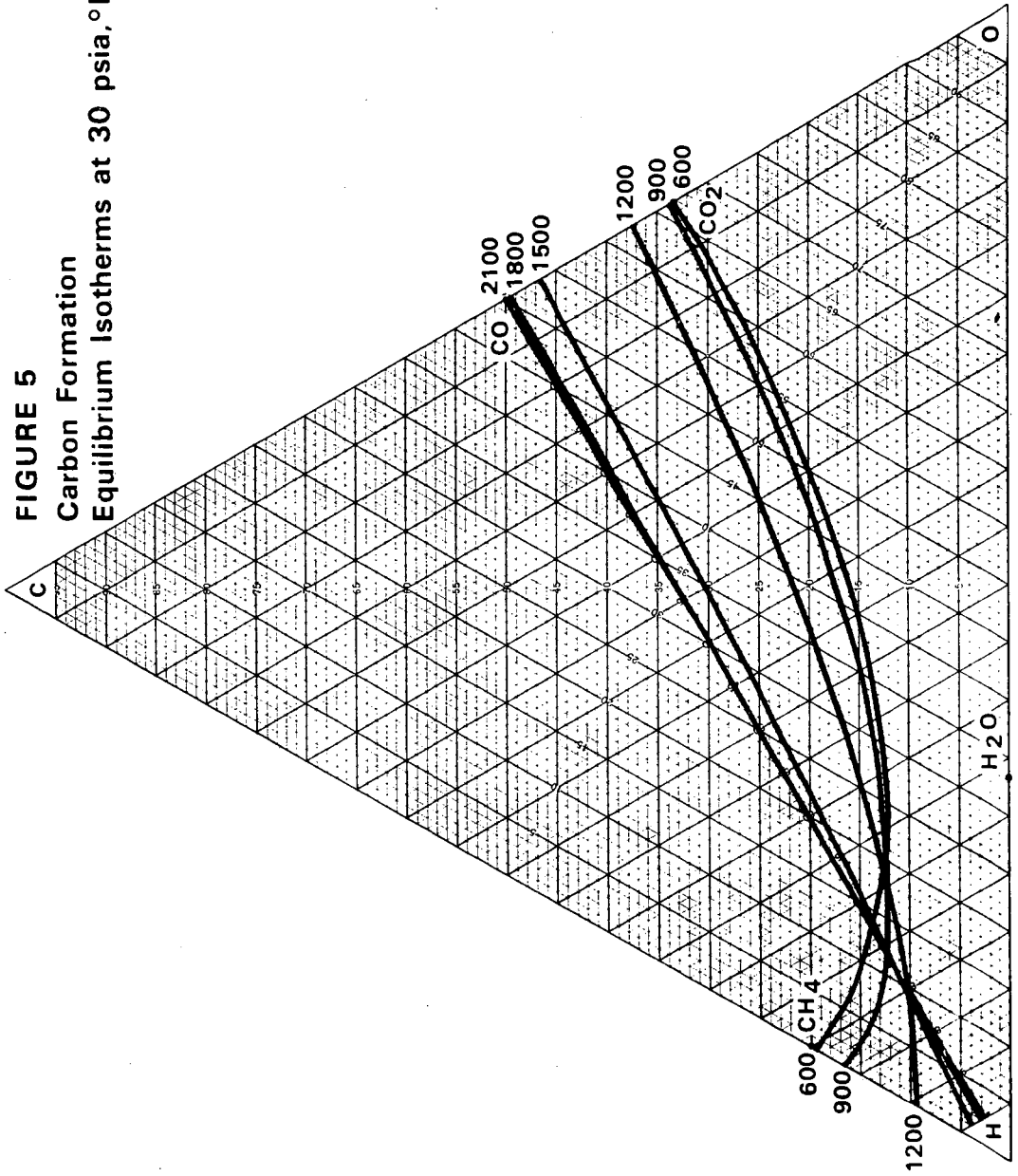
Reactor No.	Feed	-----Outlet-----					
	<u>1</u>	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>	<u>5</u>	<u>6</u>
Composition, Vol %							
H <sub>2</sub>	49.80	54.38	50.36	46.50	36.29	24.00	12.05
CO	49.80	25.37	20.42	16.27	8.24	2.69	0.49
CO <sub>2</sub>	0.10	17.29	21.99	26.06	34.62	41.83	46.45
CH <sub>4</sub>	<u>0.30</u>	<u>2.96</u>	<u>7.23</u>	<u>11.17</u>	<u>20.85</u>	<u>31.48</u>	<u>41.01</u>
	100.00	100.00	100.00	100.00	100.00	100.00	100.00
Steam/Gas	0.48	0.29	0.33	0.36	0.47	0.62	0.78
Pressure, psia	62	57	50	43	36	29	22
Temperature °F	900	1373	1259	1180	1037	884	718

**FIGURE 4**  
**Element Coordinates**  
**Raw Materials, Intermediates and Products**

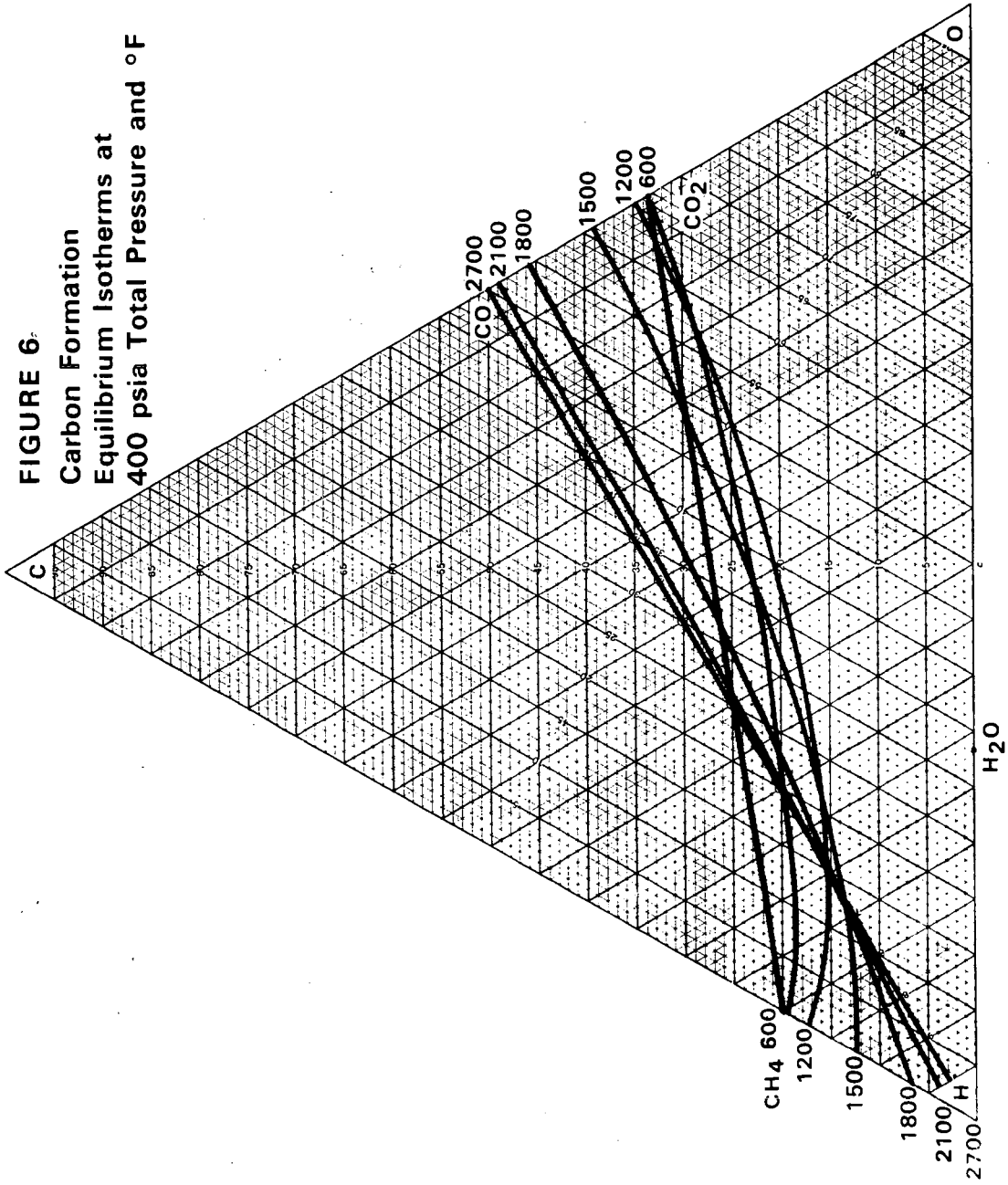




**FIGURE 5**  
**Carbon Formation**  
**Equilibrium Isotherms at 30 psia, °F**



**FIGURE 6:**  
Carbon Formation  
Equilibrium Isotherms at  
400 psia Total Pressure and °F



**FIGURE 7**  
**Carbon Formation Isotherms at**  
**400 psia Total Pressure and °F**  
**▽ RMPProcess**

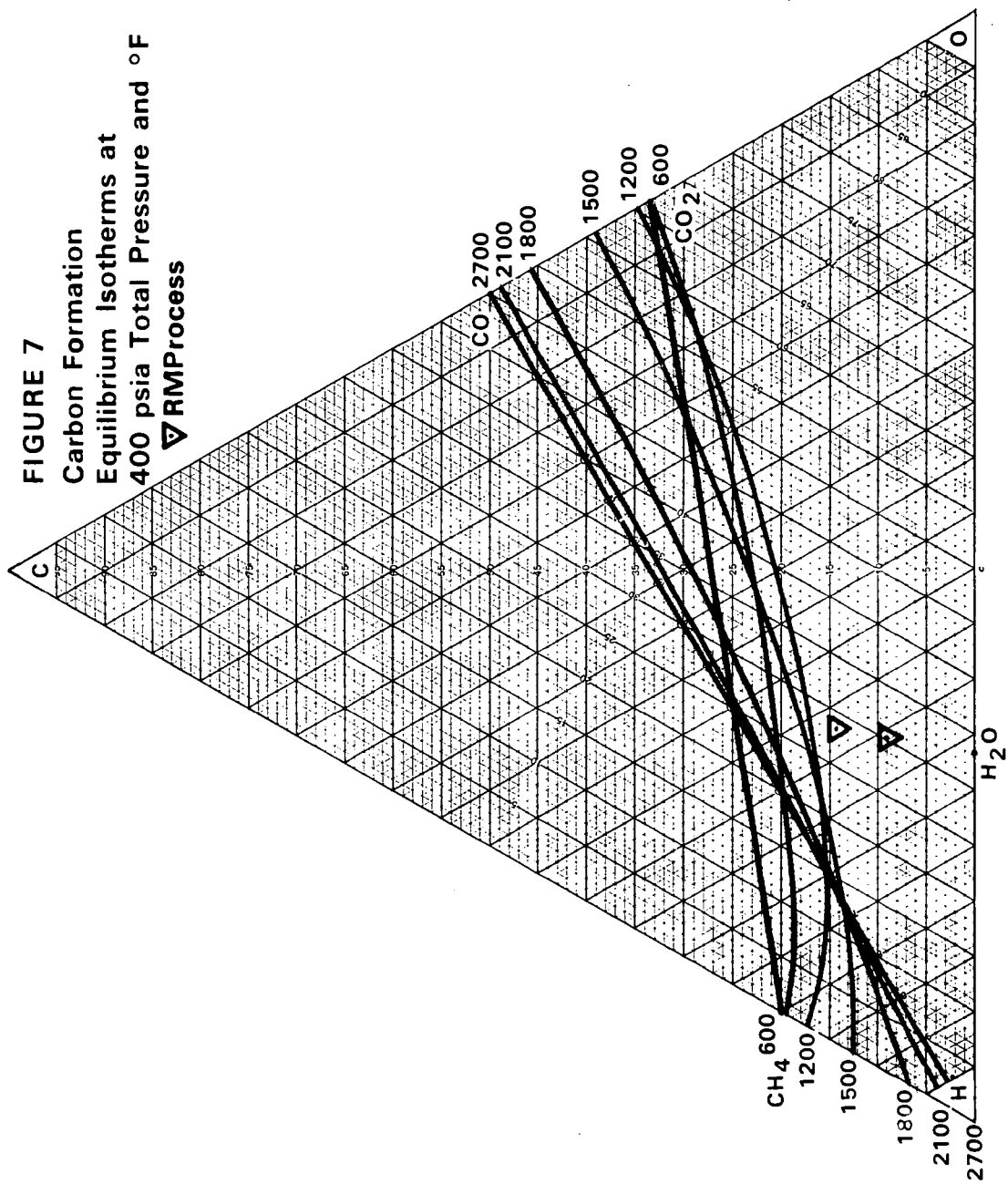


FIGURE 8

Carbon Formation  
Partial Equilibrium Isotherms at  
270 psia Partial Pressure of Hydrogen,  
Carbon Monoxide, Carbon Dioxide and  
Steam and °F

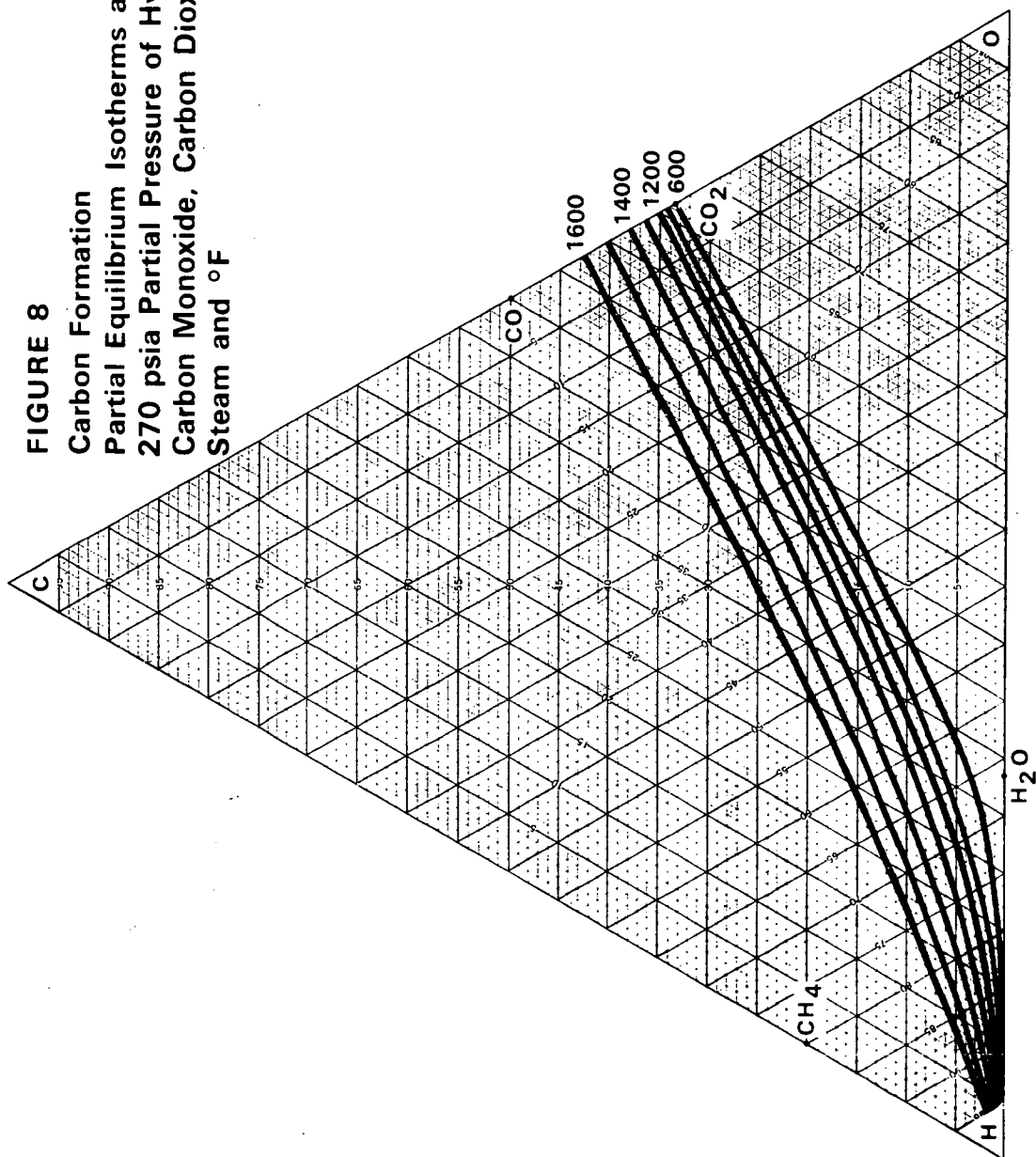


FIGURE 9 - FINAL STAGE OF METHANATION

